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(54) Title: WEAR-RESISTANT LAMINATED ARTICLES (57) Abstract In a wear-resistant laminated article (e.g. a bearing, or a compressor rotor blade) made by heating an assembly of superimposed layers of fabric impregnated with a phenolic or other thermosetting resin, the fabric is made of non-asbestos yarn comprising a core of glass fibre with a surface of aramid fibre and a relatively porous fibre such as viscose fibre, the aramid fibre forming not more than 40 % by weight of the yarn. The laminate may further incorporate carbon fibres.		

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Wear-Resistant Laminated Articles

This invention relates to wear-resistant laminated articles, such as bearings, and rotor blades for pumps and compressors.

Well-known articles of this kind are made by heating an assembly of superimposed layers of cloth made of asbestos yarn and impregnated with a thermosetting resin.

The present invention is concerned with avoiding the use of asbestos.

It is already known (see for example GB-A-2 121 844) to make wear-resistant laminated articles using, instead of resin-impregnated asbestos cloth, heat-resistant aramid fibres, that is to say fibres of poly(aromatic amide), or glass fibres, made with an organic binder into flexible sheet material by a paper-making process, the sheet being

then impregnated with resin. However, to obtain articles capable of sustained operation above 175 °C, and in particular at temperatures up to 200 °, there has to be used a proportion of aramid fibre which makes the product too expensive. If glass fibre is used instead of aramid fibre, the article is extremely abrasive.

According to the present invention there is provided a wear-resistant laminated article made by heating an assembly of superimposed layers of fabric impregnated with thermosetting resin, in which the fabric is made of non-asbestos yarn comprising a core of glass fibre with a surface of aramid fibre and a relatively porous fibre, the aramid fibre forming not more than 40% by weight of said yarn.

Fabric made of such non-asbestos yarn is commercially available as thermal insulation and packing, the relatively porous fibre therein being viscose. The function of the viscose fibre in the practice of the present invention is to assist impregnation with thermosetting resin of the fabric of glass core fibre/aramid surface fibre. The fabric is preferably woven, but may be of knitted construction.

The aramid fibre employed can be all of the para-form, such as that sold under the trade mark KEVLAR, but up to

half of the aramid can if desired be contributed by meta-form such as poly(m-phenylene-iso-phthalamide).

A preferred composition of the yarn is

Glass fibre	:	50-75, particularly 50-70%
Aramid fibre	:	5-35, particularly 15-35%
Viscose fibre	:	5-25, particularly 10-25%

these proportions being by weight of the yarn. It is further preferred that the fabric should have a weight per unit area in the range 550-900 grams/m².

A friction modifier such as graphite, polytetrafluorethylene or molybdenum disulphide at levels from 2 to 20% by dry weight of the thermosetting resin may if desired be included to improve the wear-resistance of the product.

Suitable thermosetting resins are phenolic resins, such as phenol-formaldehyde resins derived from phenol itself or a hydrocarbon-substituted phenol.

For certain applications such as very heavy duty compressor blades, the novel wear-resistant articles described above may lack sufficient stiffness.

To remedy this, carbon fibres may be incorporated into the laminate. This may be accomplished by interleaving the fabric layers with layers of a carbon fibre resin pre-preg material, prior to lamination into an article. The carbon fibre may be in the form of a woven cloth or a non-woven felt, although the former is preferred. The resin is preferably the same as the resin used to impregnate the fabric, a phenolic resin being particularly preferred. The carbon fibre content may be in the range of from 5 to 30% by weight, more preferably in the range 10 to 25% by weight.

The phenolic resin may contain from 2-10% by weight of an epoxy resin material, together with a hardener for the latter, in order to promote adhesion to the carbon fibres. An epoxy resin content of about 5% by weight is particularly preferred.

The carbon fibres may also be blended into the fabric as an integral component thereof. For example, a carbon fibre weft may be used in making the fabric. In some circumstances, this latter approach may be preferable to incorporation immediately prior to lamination because it results in a more uniform distribution of the carbon fibre reinforcement.

The invention is further illustrated by the following Example.

EXAMPLE ONE

A plain weave cloth of nominal thickness 2mm, weight per unit area 620 grams/m², and a construction of 80 ends per dm and 36 picks per dm, of the kind sold for protection against splashed molten metal, was impregnated with a solution (50% by weight solids content) in mixed ethanol/methanol/water (86% ethanol, 4% methanol by weight) of a conventional phenol-formaldehyde resol sold by British Petroleum Chemicals Limited under the trade mark CELLOBOND. The cloth itself was woven from glass-core yarn (E-glass fibre), with aramid fibre and viscose wrapped round the glass core. Total composition was: glass, 54%, aramid, 34%; viscose, 12%.

Excess resin solution was squeezed from the impregnated cloth by passing it between rollers, and the sheet was then heated at 135° for 20 minutes to remove solvent present in the retained resin solution and to part-cure the resin.

Sheet laminate

From the material obtained as described above 8 pieces measuring 300 x 300 mm were cut. The 8 pieces were superimposed one upon another (with the weft of adjacent pieces at right angles). The assembly was then cured at 150°C in a steam-press (pressure 7.7 MPa; time 45 mins) and then post-cured at 150°C in air.

The laminate thus formed is readily machinable to form pump or compressor rotor blades. Its properties are given later in this specification.

Tubular laminate

The part-cured cloth was wrapped onto a heated mandrel (100°C) of diameter 20mm, and the tubular laminate produced was compression moulded and then baked in an oven at 150°C to cure the resin fully.

The tubular laminate is readily converted into the form of bushes. The properties of the tube and of bushes machined from it are given later in this specification.

Sheet Properties

<u>PHYSICAL PROPERTY</u>	<u>Material according to the invention</u>	<u>Known asbestos laminate</u>
Room temperature		
flexural strength	140 MPa	97 MPa
Flexural strength at 200°C following 4 days aging at 200°C	115 MPa	70 MPa
Flexural strength at 200°C following 10 days aging at 200°C	90 MPa	60 MPa
Compressive strength	255 MPa	312 MPa
Tensile strength	92 MPa	67 MPa
Notched Charpy impact strength	46 KJ/m ²	20 KJ/m ²
Density	1.52gram per c	1.73gram per cc
Shear strength	107 MPa	93 MPa
Bond strength	5.3 KN	5.5 KN
Water absorption		
at 6.35mm thickness	600 mg	170 mg
Linear coefficient of thermal expansion per °C	18 x 10 ⁻⁶	13.5 x 10 ⁻⁶
Flexural modulus	6.72 GPa	13 GPa

These physical properties, especially the flexural strength and thermal expansion, show the material to be particularly suitable for use in rotor blades, for example in a rotary compressor.

The material of the invention showed dimensional stability in oil similar to that of the asbestos laminate: both materials shrank in length by 0.05% when soaked in hot oil at 125°C for 24 hours.

Comparative wear tests were carried out using equipment designed by the National Centre of Tribology and manufactured by Chloride Ferostatics. In this the test sample is in the form of a pin which is held under a fixed load against a rotating counter-face sleeve mounted on a shaft. Lubricated conditions were simulated by using test samples previously soaked in oil for 72 hours. The wear of the samples was assessed by measuring the width of the resulting scar damage. The material of the invention and the asbestos laminate were tested under identical conditions and both yielded scars 3mm wide. (A laminate consisting of a cloth of 100% glass fibre impregnated with phenolic resin gave a scar of 11mm).

Tube Properties

<u>PHYSICAL PROPERTY</u>	Material according <u>to the invention</u>	Known asbestos <u>laminate</u>
Density	1.52 g per cc	1.66g per cc
Compressive strength	225 MPa	280 MPa
Axial coefficient of linear expansion per °C	12.8 x 10 ⁻⁶	11.7 x 10 ⁻⁶

The following investigations of friction and wear were run dry without external lubrication.

Scar wear

The sample in the form of a strip is held against a rotating shaft of EN32 case-hardened steel under a fixed load for 100 hours continuously, and the width of the resulting scar damage is measured. The following results were obtained:-

<u>Material</u>	<u>Scar wear (mm)</u>
1. According to the invention	9.5
2. Asbestos laminate	14.3
3. <u>1</u> additionally containing graphite (10% by weight)	6.2
4. <u>2</u> additionally containing graphite (10% by weight)	9.8

Friction velocity test

This uses a reciprocating rig in which a loaded sample slides horizontally against a mild steel counterface. Both load and reciprocating speed can be varied. The frictional force is measured using a load cell sensor. The results given below compare the frictional behaviour of the material of the invention with that of an asbestos laminate under a load of 5kg.

Friction coefficient

<u>Velocity</u> (cm per min)	Material according	Known
	<u>to the invention</u>	<u>asbestos laminate</u>
0.2	.42	.46
0.8	.41	.54
1.5	.43	.60
3	.44	.64
6	.49	.66
12	.47	.75
24	.46	.68
32	.51	.66

Pressure velocity (PV) test

In this, housed machined bushes are run against a shaft at varying speeds over a range of pressures. A particular test would be carried out at constant speed with the load being progressively increased. At each load the temperature of the bush is monitored. Once this temperature has reached a maximum value, the load is increased and so on until the bush fails mechanically. A

limiting PV value can be calculated. Bushes were prepared from the material of the invention and from the asbestos laminate and tested; results are shown below.

Limiting PV value (kg/cm² x m/min)

Speed (metres per min)	Material according to the invention	Known asbestos laminate
20	350	235
60	470	350

The friction and wear test results given above show the material of the invention to be a useful high temperature bearing material, suitable for the replacement of bearings currently manufactured from asbestos yarn.

EXAMPLE TWO

To illustrate the effect of the inclusion of carbon fibres, the procedure described earlier in relation to Example one was repeated, with the addition of the step of interposing between each layer of the stack of pieces, a

ply of a square weave carbon fibre fabric of weight 836gm/m^2 woven from 20000 filament tows of 100% PAN-based carbon fibres. This fabric had been previously impregnated with a similar phenolic resin solution but in this case containing about 5% by weight of an epoxy resin comprising diglycidyl ether of bisphenol A and a minor amount of an amine hardener. This was subjected to a preliminary partial curing treatment prior to use. A similar ply was applied to each face of the stack and the whole press-cured as before. The carbon fibre content of the product was about 16% by weight.

On testing the modified laminate of this Example, the physical properties were found to be improved in certain respects over those of Example one, as follows:-

Room temperature flexural strength	175 MPa
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Flexural strength at 200°C after 4 days ageing at 200°C	140 MPa
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Flexural modulus	15 GPa
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Bond strength	5 KN
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Linear coefficient of thermal expansion per °C	11.34×10^{-6}
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EXAMPLE THREE

The procedure of the first example was followed, but this time using a cloth in which the weft yarn also included a carbon fibre component. Pieces were cut from the cloth and made into a laminate which was then press-cured. The product had significantly better properties than Example one, but in this case, the carbon fibre component was more uniformly distributed throughout the product.

EXAMPLE FOUR

Example two above was repeated using plies of non-woven carbon fibre tissue instead of woven fabric, the pre-treatment with resin remaining as before. The product had better properties than Example one, but was not quite as good as Example two.

The improved physical properties, especially the flexural strength and thermal expansion, show the carbon fibre modified material to be particularly suitable for use as rotor blades, particularly for use in heavy duty applications such as in certain kinds of rotary compressor.

CLAIMS

1. A wear-resistant laminated article made by heating an assembly of superimposed layers of fabric impregnated with a thermosetting resin, characterised in that the fabric is made of non-asbestos yarn comprising a core of glass fibre with a surface of aramid fibre and a relatively porous fibre, the aramid fibre forming not more than 40% by weight of the yarn.
2. An article according to claim 1, characterised in that the yarn comprises by weight glass fibre, 50-70%; aramid fibre, 15-35%; and viscose fibre, 10-25%.
3. An article according to claim 1 or claim 2 characterised in that the resin is a phenolic resin.
4. The use of an article according to any of claims 1-3, as a rotor blade.
5. The use of an article according to any of claims 1-3, as a bearing.
6. The wear-resistant laminated article of claim 1 further characterised by the inclusion of carbon fibres in an amount comprising 5 to 30% by weight.

7. An article according to claim 6 wherein said carbon fibres are incorporated by interleaving the superimposed fabric layers with layers of carbon fibre in the form of cloth or non-woven tissue impregnated with resin material.
8. An article according to claim 7, characterised in that the carbon fibres are incorporated by blending them into the fabric as an integral component thereof.
9. An article according to claim 7 or claim 8 characterised in that the carbon fibres are incorporated by blending them into at least some of the yarn used to make the fabric.
10. An article according to claim 7 wherein the resin material is the same as that used to impregnate the fabric.
11. An article according to claim 6, characterised in that the resin includes from 2-10% and preferably about 5% by weight of an epoxy resin, together with hardener therefor.
12. The use of an article according to any of claims 7-11 as a rotor blade.

AMENDED CLAIMS

[received by the International Bureau
on 4 October 1990 (04.10.90);
original claims 1-12 replaced by amended claims 1-12
(2 pages)]

1. A wear-resistant bearing material made by heating an assembly of superimposed layers of fabric impregnated with a thermosetting resin, characterised in that the fabric is made of non-asbestos yarn comprising a core of glass fibre with a surface of aramid fibre and a relatively porous fibre, the aramid fibre forming not more than 40% by weight of the yarn.
2. A material according to claim 1, characterised in that the yarn comprises by weight glass fibre, 50-70%; aramid fibre, 15-35%; and viscose fibre, 10-25%.
3. A material according to claim 1 or claim 2 characterised in that the resin is a phenolic resin.
4. The use of a material according to any of claims 1-3, as a rotor blade.
5. The use of a material according to any of claims 1-3, as a bearing.
6. The wear-resistant bearing material of claim 1 further characterised by the inclusion of carbon fibres in an amount comprising 5 to 30% by weight.

7. A material according to claim 6 wherein said carbon fibres are incorporated by interleaving the superimposed fabric layers with layers of carbon fibre in the form of cloth or non-woven tissue impregnated with resin material.
8. A material according to claim 7, characterised in that the carbon fibres are incorporated by blending them into the fabric as an integral component thereof.
9. A material according to claim 7 or claim 8 characterised in that the carbon fibres are incorporated by blending them into at least some of the yarn used to make the fabric.
10. A material according to claim 7 wherein the resin material is the same as that used to impregnate the fabric.
11. A material according to claim 6, characterised in that the resin includes from 2-10% and preferably about 5% by weight of an epoxy resin, together with hardener therefor.
12. The use of a material according to any of claims 7-11 as a rotor blade.

STATEMENT UNDER ARTICLE 19

The claims have been amended in the light of the International Search Report to more clearly distinguish the invention from the prior art.

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 90/00614

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁵ : C 08 J 5/04, B 29 C 67/14		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC ⁵	C 08 J, B 29 C	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	EP, A, 0050855 (HITACHI CHEM. et al.) 5 May 1982 see page 2, lines 10-16, line 22 - page 3, line 24; claims 1-10 --	1-3,5-11
Y	GB, A, 788793 (ROBERT BOSCH GmbH) 8 January 1958 see very specially page 1, left-hand column, lines 15-42; claims --	1-3,5
Y	Patent Abstracts of Japan, volume 11, no. 191 (M-600)(2638), 19 June 1987, & JP, A, 62017435 (FCC K.K.) 26 January 1987 see the abstract --	1-3,6-11
A	Patent Abstracts of Japan, volume 9, no. 63 (M-365)(1786), 20 March 1985, & JP, A, 59198119 (TOUKIYOU SHIITO K.K.) 9 November 1984 ./.	1,3,6-11
<p>¹⁰ Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
18th July 1990	17. 08. 90	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	M. SOTELO	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, " with indication, where appropriate, of the relevant passages	Relevant to Claim No.
	see whole abstract; figures 2-4 from patent --	
A	Patent Abstracts of Japan, volume 11, no 60 (C-405)(2507), 24 February 1987, & JP, A, 61218636 (NIPPON VALQUA IND LTD) 29 September 1986 see the abstract --	1,3,6-11
A	FR, A, 2379376 (T.V.T. - TECHNIQUE DU VERRE TISSE) 1 September 1978 see page 3, lines 3-6; claims; figures --	1,6
A	GB, A, 2121844 (T AND N MATERIALS RESEARCH LTD) 4 January 1984 (cited in the appliation) -----	1,4,12

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

GB 9000614
SA 36527

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 09/08/90
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A- 0050855	05-05-82	JP-A- 57072847	07-05-82
		JP-A, B 57074149	10-05-82
		JP-A, B, C 57074150	10-05-82
		US-A- 4446191	01-05-84

GB-A- 788793		None	

FR-A- 2379376	01-09-78	None	

GB-A- 2121844	04-01-84	AU-B- 554034	07-08-86
		AU-A- 1449083	15-12-83
		EP-A, B 0096962	28-12-83
		US-A- 4548678	22-10-85
